

Experiment title:Absolute Structure Determination by
Three-Beam Diffraction**Experiment****number:**

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The term absolute structure (Jones, 1986, Burzlaff & Hümmer, 1988) has different meanings in different point groups. For chiral point groups it means the determination of the absolute configuration of chiral molecules. In case of achiral molecules it is the absolute conformation. For polar point groups it means fixing the structure with respect to the the polar direction. For non-centrosymmetric point groups with roto-inversions 4 or 6 it means an assignment of absolute axes. The traditional method to determine the absolute structure is to exploit the violation of Friedel's law due to anomalous dispersion effects. Problems, however, occur in case of light atom structures where anomalous dispersion effects become too weak.

In principle the determination of the absolute structure reduces to the determination of the sign of structure factor phases. By means of a three-beam interference experiment the sign and the modulus of triplet phases $\Phi_T = \varphi(-h) + \varphi(g) + \varphi(h - g)$ can be determined (Hümmer & Weckert, 1995). Therefore, best selectors between the enantiomorphic forms are triplet phases close to 90°. This method works without any use of anomalous dispersion effects.

As part of a project of the 'Apparatus Commission of the IUCr' on 'Absolute Structure Determination of Light Atoms Structures' four compounds with very small anomalous dispersion effects were investigated by three-beam diffraction experiments.

1. BN (boron nitrite), cubic, spacegroup $F43m$: This compound serves as a model for structures with small anomalous dispersion effects. Assuming $x = y = z = 0$. O for the coordinates of the B atom, two positions for the N-atom are possible, namely $x = y = z = 0.25$ or $x = y = z = 0.75$. By

measured triplet phases an absolute axis system could be assigned by three measured triplet phases each indicating the same absolute structure. The correct coordinate for the N atom is $x=y=z=0.75$.

2. $C_{16}H_{24}N_2O$ is a chiral drug which crystallizes in space group $P2_1$. The absolute configuration of this molecule could be determined by refining an enantiomorph sensitive parameter (Flack, 1983) from an intensity data set measured with Cu K_α radiation. The standard deviation of this parameter however indicates, that the inverse structure cannot be ruled out from a statistical point of view. By measured triplet phases the refined absolute configuration could be confirmed unambiguously.
3. $C_{28}H_{20}N_2$ is an achiral molecule which crystallizes in space group $S'2_12121$. The absolute conformation of the molecule could be determined by three-beam diffraction. It was impossible to fix the absolute conformation of this molecule by anomalous dispersion effects from intensity measurements with Cu K_α radiation. To our knowledge the determination of the absolute structure of a compound with a C :N ratio of 14 has never been achieved before. Interference profiles of this compound are given in Fig. 1.
4. Benzil ($C_{14}H_{10}O_2$) is also an achiral compound. The space group could be determined to be $P3_221$. This crystal of benzil was available as a (0 0 1) plate. All investigated crystals of benzil show this absolute structure independent of the condition of growth. As the molecule itself is not chiral both absolute structures should be possible with the same probability. This preference of only one absolute conformation is not understood so far.

These experiments show that the absolute structure of crystals with weak anomalous dispersion effects can be determined by three-beam diffraction experiments provided that crystals with sufficient low mosaic spread are available.

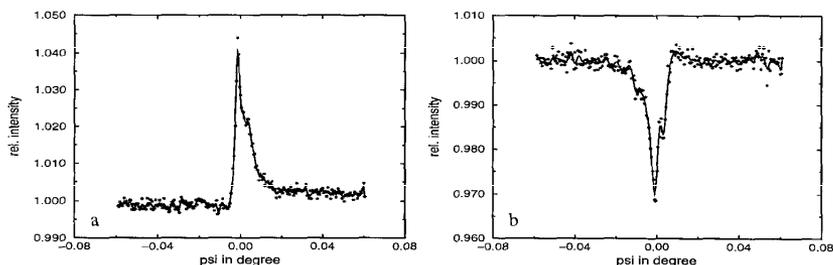


Figure 1: Measured three-beam V-scan profiles with an estimated triplet phase of $\mp 110^\circ$ from $C_{28}H_{20}N_2$ (space group: $P2_12_12_1$) at $\lambda = 1.048\text{\AA}$; a: three-beam case: $0\ 32/72^-$, $\Phi_3^{alc} = -107.8^\circ$, b: three-beam case: $0\ 32/2^-2^-$; $|F(0\ 3\ 2)| = 36$, $|F(\bar{2}\ 2\ \bar{2})| = 70$, $|F(2\ 1\ 4)| = 45$.

References

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